OPTION A: ANALYTICAL CHEM
A5 – NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

IB Chemistry

TAD04

A5 – NMR Spectroscopy

- A.5.1 Deduce the structure of a compound given information from its 1H NMR spectrum. (3)
  - *Students will only be assessed on their ability to deduce the number of different hydrogen (proton) environments and the relative numbers of hydrogen atoms in each environment. They should be familiar both with a word description of a spectrum and with a diagram of a spectrum, including an integration trace. The interpretation of splitting patterns will not be assessed.*
- A.5.2 Outline how NMR is used in body scanners. (2)
  - ***Aim 8:*** *Protons in water molecules within human cells can be detected by magnetic resonance imaging (MRI), giving a three-dimensional view of organs in the human body.*

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Review of Quantum Numbers

- The Quantum Theory helps describe how electrons are organized in the atom by using 4 distinct numbers. They help to describe where electrons are most likely to be found.
  1. Principal Quantum Number (n)
  2. Angular-momentum quantum Number (l)
  3. Magnetic Quantum Number (M_l)
  4. Magnetic Spin (M_s)

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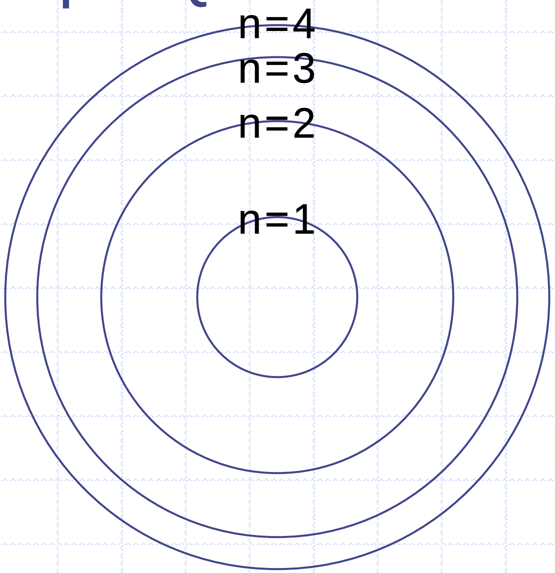
1. Principal Quantum Number (n)

- Always positive (n=1,2,3,4,5, etc)
- In turn, the distance between the electrons and the nucleus become farther apart.
- Since it takes energy to separate a negative charge from a positive charge, the increased distance between the nucleus and the electron means that the energy of the electron increases along with the Principal Quantum Number.



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2. Angular-momentum Number (l)

- This is the number that defines the **dimensional shape** of the orbital. Orbitals are grouped into different subshells/levels, these are classified under the following groups s, p, d, f.
- For example:

l = 0 → s

l = 1 → p

l = 2 → d

l = 3 → f

l = 4 → g

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3. Magnetic Quantum Number (M_l)

- This number describes which orbital an electron is most likely to be found. If an orbital that has an angular-momentum number of 1, the magnetic quantum numbers can have any integral number from -1 to 1.
- For Example:
  - If l = 0, then M_l = 0
  - If l = 1, then M_l = -1 0 +1
  - If l = 2, then M_l = -2 -1 0 +1 +2
  - If l = 3, then M_l = -3 -2 -1 0 +1 +2 +3

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Electron Spin (M_s)

- Electrons behave as if they were spinning around an axis, much as the earth spins daily but both directions
  - + ½ Spin (up) = if clockwise
  - - ½ Spin (down) = then counterclockwise
- Just like electrons have a spin and spin number, so do protons
  - It is this principle that will be used to determine shape and composition of compounds through NMR spectroscopy

Structure via NMR

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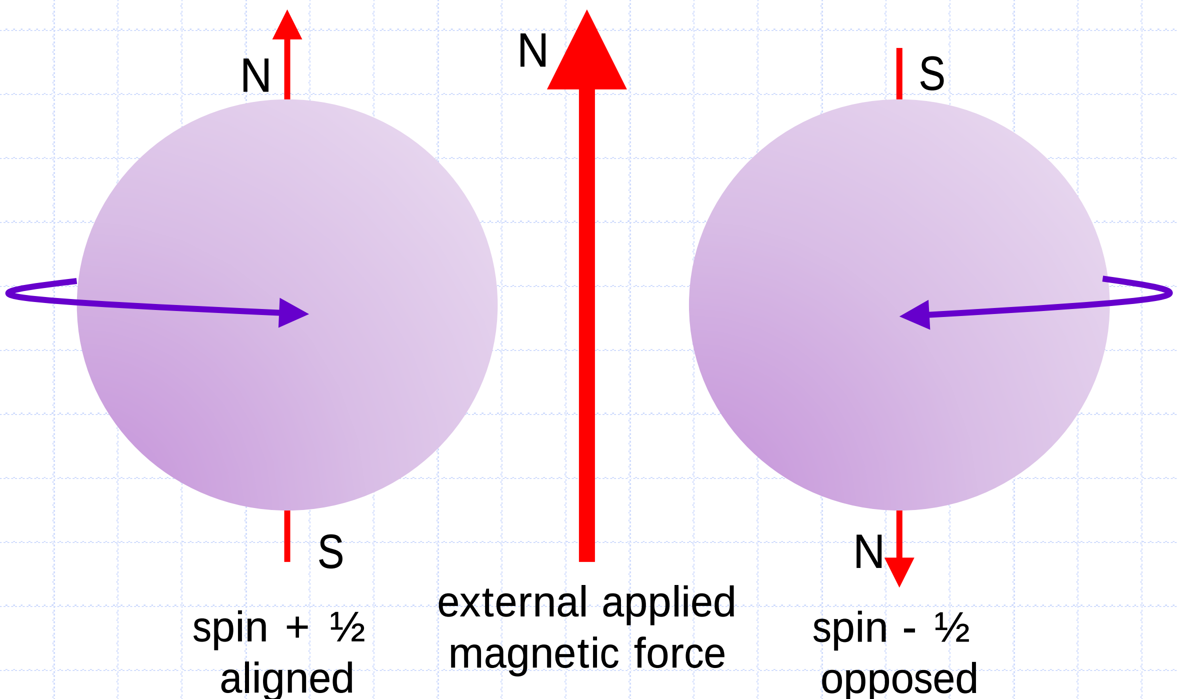
A.5.1 Deduce the structure of a compound given information from its 1H NMR spectrum. (3)

- Nuclear Magnetic Resonance (NMR) is a spectroscopic technique which takes advantage of the spin of atomic nuclei.
- Visible nuclei must contain an odd number of protons, neutrons, or both (^{1}H, ^{19}F, ^{31}P, etc)

Proton can spin clockwise or counter-clockwise. Use right-hand rule for the magnetic field



The ±½ represents the spin quantum number

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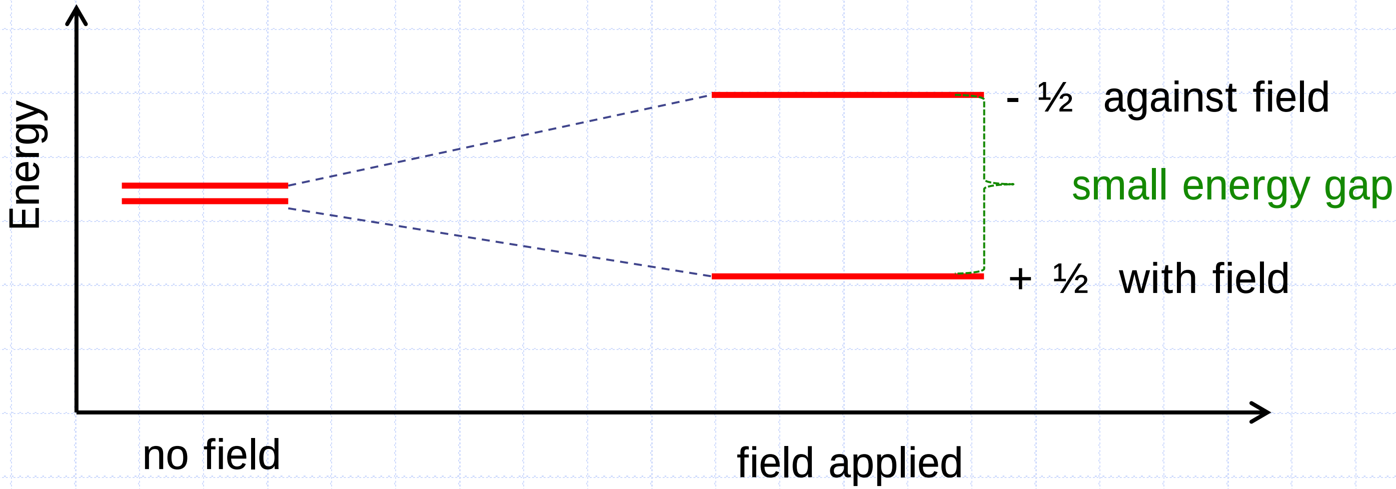
Energy of Spin

- Without a magnetic field, the spins would cancel each other out
- With a magnetic field, they align with or against the field depending on their spin
  - With field (parallel) = low energy, greater abundance
  - Against field (anti-parallel) = high energy, low abundance



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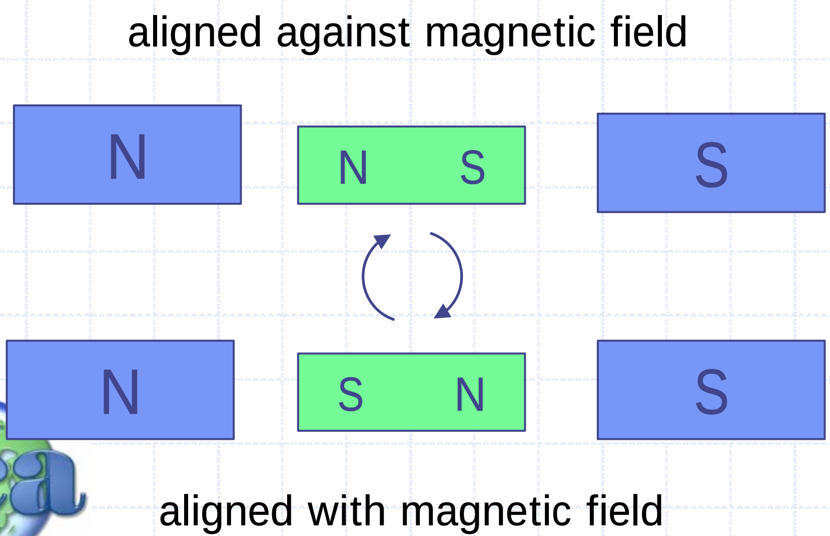
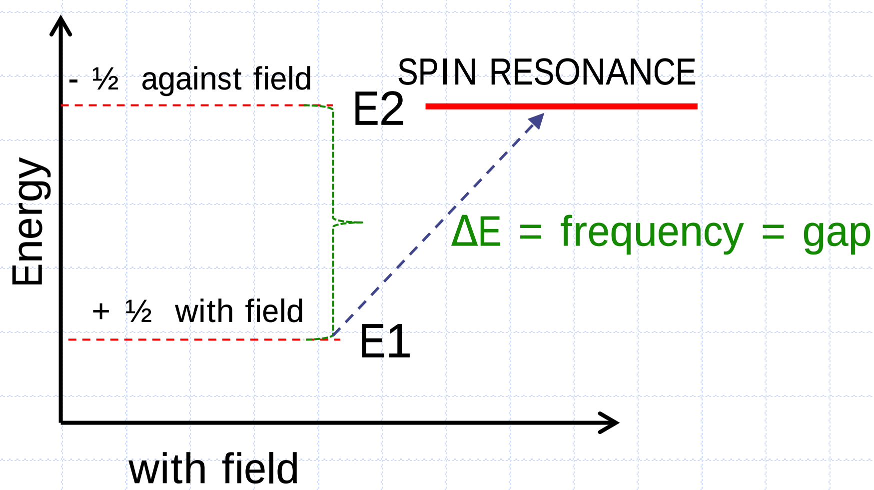
Applied NMR Spectrum: Spin Resonance

- In NMR it's easier to analyze a sample that does not generate its own NMR spectrum. **Spin resonance** can be achieved by the addition of a EM frequency equal to the small energy gap. When matched..
  - the material "flips over"
  - its generally 200-600 MHz (low frequencies)

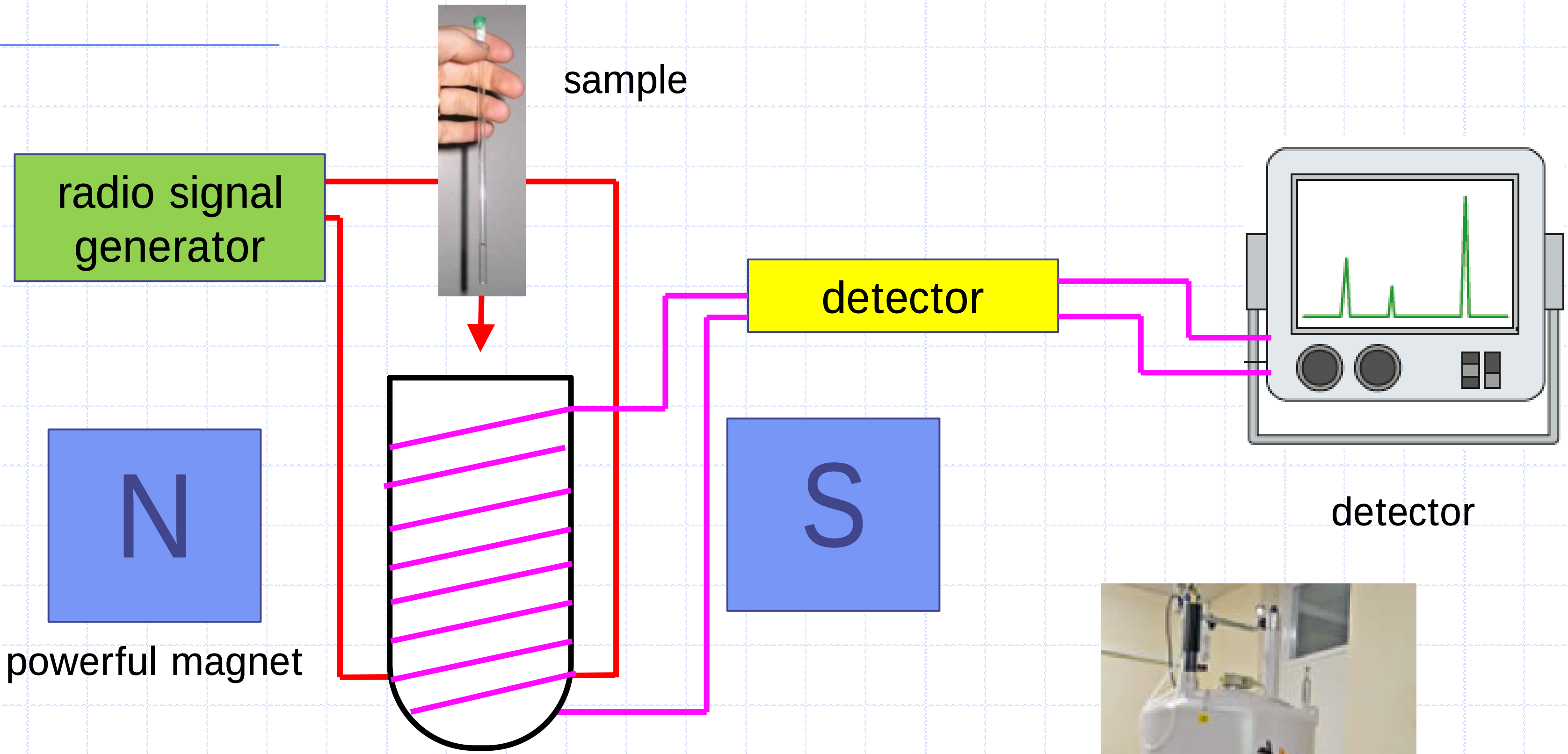




Sample Prep and Collection

- Sample is dissolved in solvent
- Less complicated if solvent does not generate its own NMR spectrum
- Loaded in a glass tube (NMR tube) transparent to radio waves
- Tube lowered into magnetic field and spun rapidly and smoothly
- Sample radiated with a pulse of various radio frequencies
- When the radio wave pulse equals that of the energy gap between nuclear spin states, the molecules in the sample absorb the waves
- Principle detector records the difference in the original signal and that it receives, causing an absorbance peak

NMR Spectrometer



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NMR Data Processing

- All elements equally bound, result in equal peaks
  - Ex. CH_4 only gives one peak for ^1H NMR
- Different arrangements provide different NMR peaks
  - Occurs because nuclei are shielded by other electrons differently
  - Ex. CH_3-CH_2-CH_2-CH_3 gives two peaks
    - Terminal Hydrogen (-CH_3)
    - Methylene Hydrogen (-CH_2-)
- Since they are shielded differently, the energy gaps (ΔE) differ and give peaks at different frequencies
  - If a reference is known, the results can simply be compared. The reference used is **tetramethylsilane (TMS).** TMS gives a ^1H NMR zero peak

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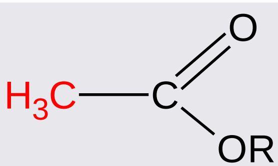
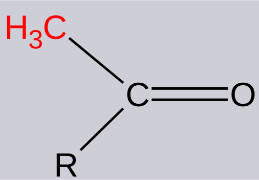
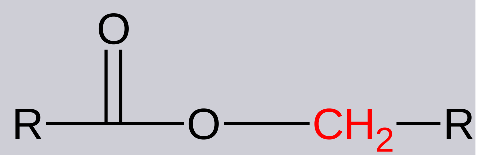
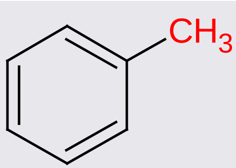
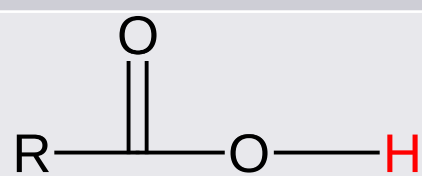
Chemical Shift of H in Compounds

- **Chemical Shift:** The extent to which the other hydrogen atom (proton) signals differ from the TMS signal (symbol δ)
- The chemical shift is defined as:
  - $$\delta = \frac{(frequency\ of\ signal - frequency\ of\ TMS)x\ 10^6}{frequency\ of\ TMS}$$
    - Unit = parts per million - ppm (hence x10^6)
- The chemical shift of various functional groups for ^1H NMR can be found in Table 18 of the Data Booklet (2009)

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
$R-CH_3$	0.9-1.0	$R-C \equiv C-H$	1.8-3.1
$R-CH_2-R$	1.3-1.4	$R-CH_2-Hal$	3.5-4.4
$H-CR_3$	1.4-1.6	$R-O-CH_3$	3.3-3.7
	2.0-2.5	$R-CH_2-OH$	3.3-4.0
	2.2-2.7		3.8-4.1
	2.5-3.5		9.0-13.0
		$R-O-H$	4.0-12.0

NMR Info and Peaks

- Three peaks, each at different chemical shifts relative to the small TMS peak at zero
  - **Integration Trace** – Step represents abundance (area under)
  - 1.0 (x3) = **H** in R-CH_3
  - 3.6 (x2) = **H** in R-CH_2-OH
  - 5.0 (x1) = **H** in R-O-H

H_3C——CH_2——OH

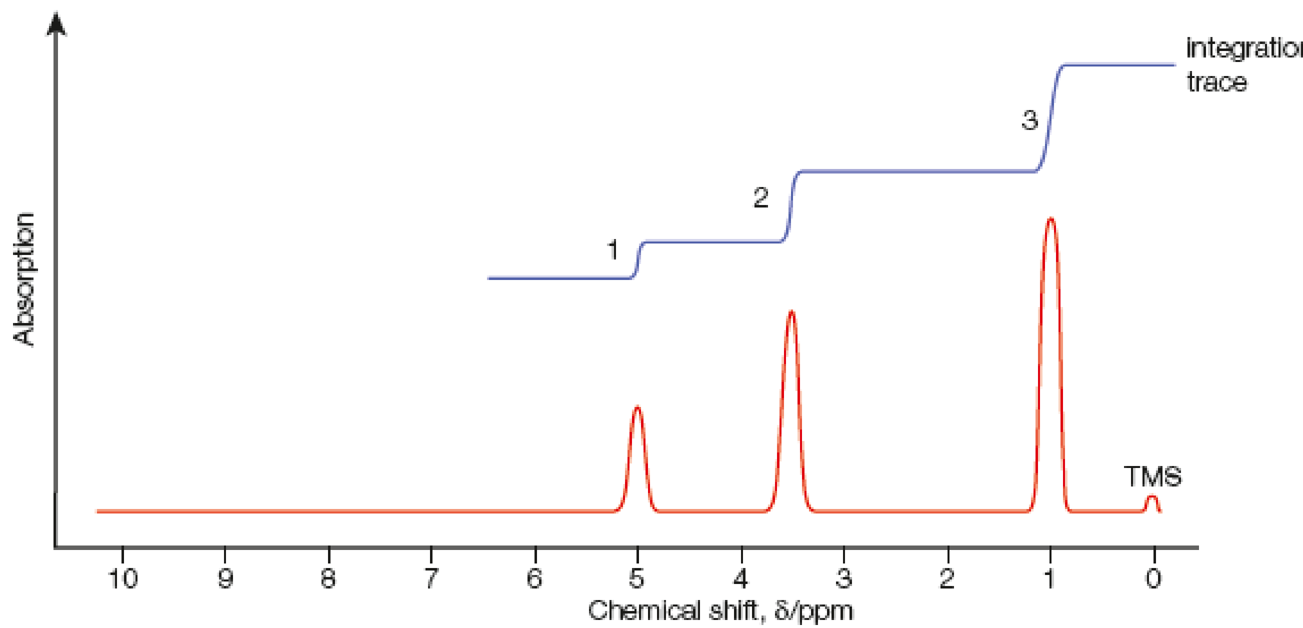
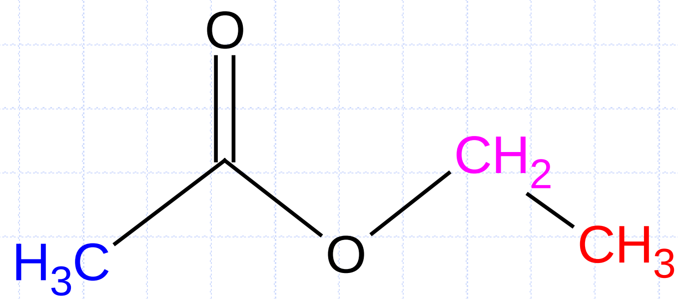
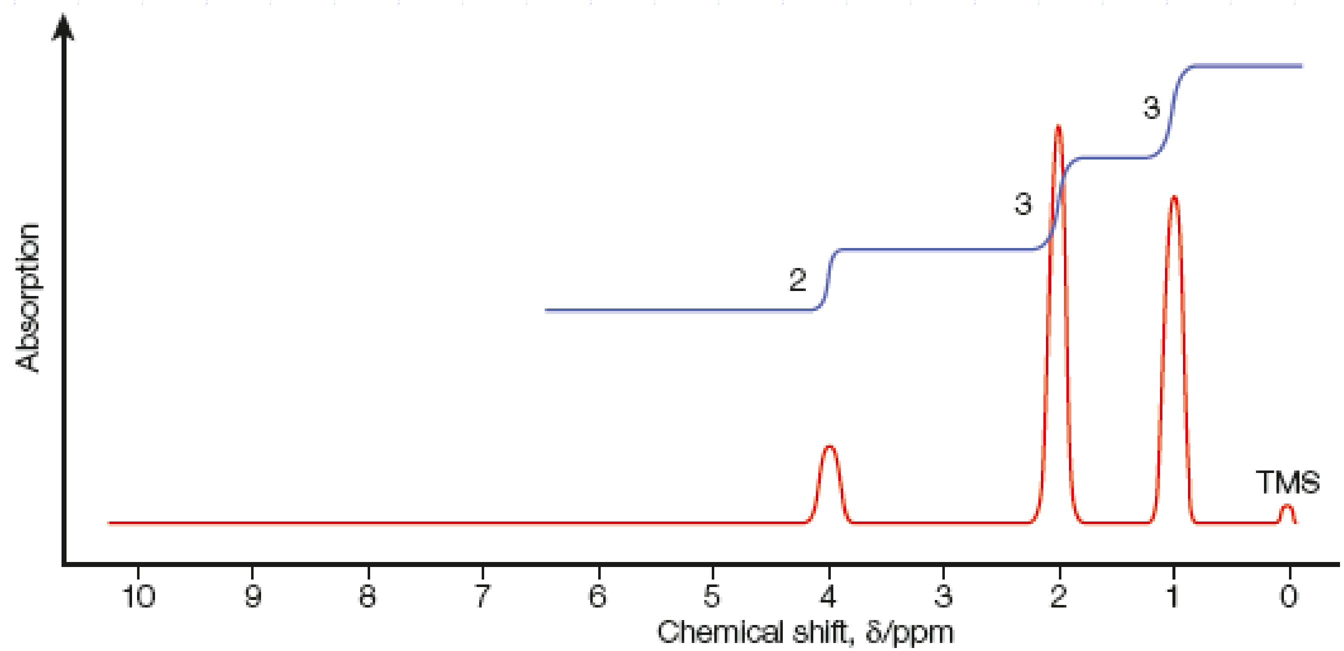


Figure 21.64 The low-resolution [1]H NMR spectrum of anhydrous ethanol showing peaks and **integration trace**

Determine the Structure of the Isomer

- The data below is of a compound with a molecular formula of **$C_4H_8O_2$** determined via Mass Spec. Suggest the structure of A:
  - 1.0 (x3) = **H** in R-CH_3
  - 2.0 (x3) = **H** in CH_3-C(=O)OR
  - 4.0 (x2) = **H** in RCH_2-O-C(=O)R





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NMR for MRI Scanners

A.5.2 Outline how NMR is used in body scanners. (2)

- Magnetic Resonance Imaging (MRI) uses NMR for medical diagnosis. (for obvious reasons the ‘nuclear’ part of the name was dropped)
  - Patient is placed inside a cylinder containing a very strong magnetic field
  - Radio waves cause the H-atoms in the water molecules of the body to resonate (but not as IR, V, or UV)
  - Each type of body tissue resonates differently which represents the density of H (water) in the tissue
  - Computer software translates this signal into an image

What can an MRI “see” ?

- MRI can see soft tissues
  - Blood vessels
  - Cerebrospinal fluid
  - Bone marrow
  - Muscles
- MRI cannot see
  - Bone and other materials with limited water content

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Uses for an MRI

- MRI can be used to view
  - Tumors
  - Damage caused by
    - Multiple sclerosis (MS)
    - Strokes
    - Joint injuries
    - Heart disease (via narrowing of arteries)
    - Herniated discs
- Procedure is harmless unless the patient has received metal replacements (pacemakers, joint pins, heart valves, etc)
- Patients may be given a contrast agent to help produce higher contrast images of organs and tissues

MRI Setup and Output

- The body is essentially the glass NMR tube, the data is simply a computer translated version of several peaks compared to known values